STUDIES ON THE AVAILABILITY OF MIXED FERTILIZERS. III. IDENTIFICATION OF THE CHEMICAL CONSTITUENTS IN HIGH-ANALYSIS MIXED FERTILIZERS.

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III. IDENTIFICATION OF THE CHEMICAL CONSTITUENTS IN HIGH-ANALYSIS MIXED FERTILIZERS.

By

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In the past few years, the production and the consumption of mixed fertilizers especially of high-analysis mixed fertilizers have been increasing remarkably. This is said to be due to the high concentrations of effective components, the rationality of the granular form for the fertilization and other handlings, and the higher availability of the high-analysis mixed fertilizers (1, 2). However, all the characteristics of the high-analysis mixed fertilizers were not completely examined till now. On the one hand, components of the high-analysis mixed fertilizers are growing higher and higher and their raw materials are increasingly diversified, and then the high-analysis mixed fertilizers offer to the fertilizer industry many problems to be solved such as the manufacturing methods, the fertilization techniques, the price levels, etc.

The writers have been making a series of experiments to clarify the reality of the effect of the high-analysis mixed fertilizers and to solve the different problems that confront the fertilizer community to day, such as the manufacturing methods and the fertilization techniques.

In the present paper, chemical properties of the high-analysis mixed fertilizers were examined in relation to their availabilities.

Experimental materials

About 20 kinds of representative marketed high-analysis mixed fertilizers were used for the present experiments.

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Table 1. Classification of high analysis mixed fertilizers.

I.	Sulfate-Ammonium Phosphate system
	I_1 Monoammonium phosphate as a main component.
	I_2 Diammonium phosphate as a main component.
	I_3 Magnesium phosphate as a main component.
II.	Chloride-Ammonium Phosphate system
III.	Urea-Ammonium Phosphate system
IV.	Urea-Sulfate-Ammonium Phosphate system
V.	Magnesium-Ammonium Phosphate system

These samples were classified systematically according to nitrogen sources of the employed raw materials as shown in Table 1.
SHIONOYA (1) have discussed fully the manufacturing methods and the employed raw materials of these samples.

Experimental method & Results

These samples are produced through different chemical operations during the manufacturing processes. Therefore, all the samples, which are reaction products as manufactures, seem to be constructed from different chemical constituents. These reaction product are affected not only by chemical conditions but also by physical ones during the manufacturing process. Since some close relations can be predicted between these reaction products and the availabilities of the mixed fertilizers, chemical properties of these high-analysis mixed fertilizers were analyzed by the research methods used for the studies on the low-analysis mixed fertilizers (3). The x-ray diffraction analysis and the polarization microscopic observation were performed.

(I) X-ray diffraction analysis of effective chemical constituents.

As in the case of low-analysis mixed fertilizers, standard salts which are presumed to be produced during the manufacturing process were synthesized first. The samples were compared with the synthesized standard salts by Debye-Scherrer's method by using copper as the anticathode. The identified chemical constituents are given in table 2.
$NH_4H_2PO_4$, KH_2PO_4, and $(NH_4)_2SO_4$ were identified in the sample I_1. These salts seem to be characteristic constituents of this system samples. The samples which were made from a concentrate superphosphate showed the diffraction line of $CaHPO_4$. In some parts of these samples, $CaSO_4 \cdot 2H_2O$ was detected. It seemed to be formed by the decomposition of phosphate rock with H_2SO_4 and to remain in the manufactures by imperfect filtration. The sample I_2 showed clear diffraction lines of $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, $NH_4H_2PO_4$, and K_2HPO_4. KH_2PO_4 and NH_4HSO_4, anticipated reaction products, were also nearly identified. The sample I_1 showed the inclusion of $(NH_4)_2HPO_4$ besides $NH_4H_2PO_4$ being estimated to be a

Table 2. Identified materials by x-ray analysis.

Sample	Identified salts	Nearly identified salts
I_1	$NH_4H_2PO_4$, $(NH_4)_2SO_4$, KH_2PO_4	K_2HPO_4, $(NH_4)_2HPO_4$, K_2SO_4, KCl, $CaHPO_4$, $CaSO_4 \cdot 2H_2O$
I_2	$(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $(NH_4)_2SO_4$, K_2HPO_4	KH_2PO_4, NH_4HSO_4, K_2SO_4, KCl
I_3	$MgNH_4PO_4 \cdot 6H_2O$, $NH_4H_2PO_4$ K_2SO_4, KH_2PO_4	K_2HPO_4, $(NH_4)_2SO_4$, $Mg(H_2PO_4)_2 \cdot 6H_2O$
II	$NH_4H_2PO_4$, KCl, NH_4Cl	none
III	$NH_4H_2PO_4$, KCl, $(NH_2)_2CO$, KH_2PO_4, K_2HPO_4	$(NH_4)_2HPO_4$, $(NH_2CONH)_2CH_2$
IV	$NH_4H_2PO_4$, $(NH_4)_2SO_4$, $(NH_2)_2CO$ KH_2PO_4, K_2HPO_4, NH_4HSO_4	none
V	$MgNH_4PO_4 \cdot 2H_2O$, $NH_4H_2PO_4$ KH_2PO_4, $MgSO_4 \cdot 7H_2O$	K_2HPO_4, $(NH_4)_2SO_4$, $Mg(H_2PO_4)_2 \cdot 6H_2O$

main component of this sample. The sample I_2, which are thought to contain $(NH_4)_2HPO_4$ as a main component, contained $NH_4H_2PO_4$ besides the former salt. The intensities of these salts suggested that both sample I_1 and sample I_2 actually contained larger amounts of the estimated main component salts. In the sample I_3, $MgNH_4PO_4$ was identified more clearly than $Mg(H_2PO_4)_2$ and $MgHPO_4$, the latter 2 salts have been estimated to be characteristic components of this sample. From this result, it appears that the actual formation of $Mg(H_2PO_4)_2$ and $MgHPO_4$ was low.

NH_4Cl and KCl, used as raw materials, were detected besides $NH_4H_2PO_4$ in the sample II.

In the case of the sample III, $NH_4H_2PO_4$, KH_2PO_4, and K_2HPO_4, which have been thought to be main components, and $(NH_2)_2CO$ and KCl, these are raw materials, were identified. However, of the methyleneurea complexes estimated to be characteristic for this sample, only a weak diffraction line of monomethylene-diurea was detected.

The sample IV showed the inclusion of different phosphates, $(NH_4)_2SO_4$, NH_4HSO_4, and $(NH_2)_2CO$.

In the sample V, $MgNH_4PO_4 \cdot 2H_2O$, $NH_4H_2PO_4$, and KH_2PO_4 characteristic for the sample were identified. Besides these salts, diffraction lines of $MgSO_4 \cdot 7H_2O$ and $Mg(H_2PO_4)_2 \cdot 6H_2O$, presumptive intermediate reaction products, were detected.

The above results identified or nearly detected all the salts estimated to be formed in each sample. However, some samples showed diffraction lines of salts other than the estimated characteristic salts for the samples. This suggests that chemical reactions proceed unsatisfactorily in these samples. Some other samples

showed diffraction lines of salts which are thought to get mixed as impurities. For these samples, inperfect operations for removing impurities must be pointed out.

In addition to the above identified salts, the formation of some other single and double salts are predicted naturally. Then, the further examination was made by the optical method with a polarization microscope.

(II) Optical discrimination of the internal structure by a polarization microscope.

The poralization microscopic observation was made according to the method used for the examination of the low-analysis mixed fertilizers (8).

Each sample was observed by the used of an orthoscope at 100 magnifications. The crystals showed clear crystalline forms were examined for extinction angles and then determined of their crystal systems.

The birefringences of the mixed fertilizers, which form complex structures constructed of mixtures of optically anisotropic constituents, were determined by interference colours by the nicol cross.

The results obtained for the each sample were shown below.

sample 1(see the photograph No. 1, this sample belongs to the type I_1): Raw materials holding their original forms dispersed in the inner part of the particles, but their amounts were small. However, the green-yellow interference colour and the medium birefringence of this sample seemed to indicate that the homogeneity of this sample is relatively high as a whole. Some parts of this sample showed the yellow-orange interference colour and the very high birefringence and the formation of a cluster of needles was observed in these parts. The characteristics of this sample are the bright yellow-orange interference colour of the outer part of the particles and the formation of ammonium phosphate in this part.

sample 2 (see photograph No. 2, this sample belongs to the type I_2): The particles of this sample showed a ring structure of fine crystals surrounding a nucleous-like crystal. It seemed that first the ammonium phosphate was formed and then $(NH_4)_2SO_4$ and others states were formed. Therefore, the formation states of these salts were heterogeneous. The interference colour by the nicol cross was yellow-orange and the birefringence was large. The homogeneity of the ring-like part surrounding the nucleous-like crystal was remarkably high. In this ring-like part, the formation of $(NH_4)_2HPO_4$ was detected. On the other hand, a part where fine lumped particles showing a dark green interference colour and including crystals, probably of $(NH_4)_2SO_4$.

sample 3 (see the photograph No. 3, this sample belongs to the type I_3): The inner composition of the particles of this sample appeared to consist of ammonium phosphate formed first and of magnesium phosphate as the secondary product. The inferference colour by the nicol cross was yellowish dark green and the birefringence was medium. Locally, a part was observed which showed the interference colour of yellow to yellow-orange. This part was undulated and the formation of the

secondary salt was certified.

sample 4 (see the photograph No. 4, this sample belong to the type II): Raw materials used for this sample were clearly detected in various forms. Generally, the homogeneity of this sample was low. The interference colour was dark yellow and the birefringence was low as a whole particles. But locally, a part showing the yellow interference colour and included the formed ammonium phosphate.

sample 5 (see the photograph No. 5, this sample belongs to the type III): Dispersion of indigo black crystals was easily detected in the inner part of the particles of this sample. These crystals showed optical properties remarkably different from those of the other crystalline salts and are proved to be a diatomaceous earth used as an anti-caking agent. Little amounts of crystals of urea and potassium salts used as raw materials were also detected. The interference colour by the nicol cross was green tinged with yellow-orange and the birefringence was relatively high. In the homogeneous part, no difference was observed among the times at which each of the component salts was formed. This sample contained considerably large amounts of vacant space in the particles.

sample 6 (see the photograph No. 6, this sample belongs to the type IV): Dispersion of the massive crystals was detected in the particles of this sample, but their amounts were small. These crystals were presumed to be raw materials. Generally, the homogeneity was medium. The interference colour by the nicol cross was yellowish orange-green and the birefringence was relatively high as a whole. In the homogeneous part, the formation of the ammonium phosphate state was observed. The state of formation showed a mosaic structure.

sample 7 (see the photograph No. 7, this sample belongs to the type V): The internal structure of the particles of this sample was in the state of a mixed fusion. The state was further identified to be the mixed fusion of the primary products and the secondary ones. It was estimated, that magnesium phosphate and magnesium sulfate were first formed and subsequently ammonium phosphate and magnesium-ammonium phosphate were formed as the secondary products because of the above mentioned results of x-ray diffraction analysis. The interference colour by the nicol cross was dark green and the birefringence was medium. However, the homogeneous part showed the yellow orange interference colour and contained formed ammonium phosphate.

As described above, the internal structure of the high-analysis mixed fertilizers showed the higher homogeneity of component salts and their higher purity than those of the low-analysis mixed fertilizers.

Only a little amounts of the raw materials employed for manufacturing these mixed fertilizers were detected. However, considerable differences were observed both in the states of composition and the rates of composition of their chemical constituents in each sample.

Discussion

The series of experiments were made in order to clarify the reality of the availability of the high-analysis mixed fertilizers. In this report, chemical properties of the high-analysis mixed fertilizers were examined in relation to their availabilities. The x-ray diffraction analyses revealed nearly all the presumed component salts in each sample. However, in a few samples, some presumed salts were not clearly identified. Namely, in the samples of the sulfate-ammonium phosphate system, which contains magnesium, $MgHPO_4$ and $Mg(H_2PO_4)_2$, in the sample of the urea-ammonium phosphate system methylene-urea derivatives were not detected. These results seemed to suggest that the predicted chemical reactions did not proceed satisfactory or the predicted salts were very small in amount if formed. Further, some samples included the salts thought to be impurities. For example, the samples of the sulfate-ammonium phosphate system included $CaSO_4$. The salt was presumed to be produced by acid-decomposition of rock phosphate and to remain in the sample by imperfect filtration. However, when elimination of impurities is difficult or the presence of a little amount of impurities is not so disadvantageous for the manufactures, the inclusion of some impurities is of no importance.

The polarization microscopic observations showed that the homogeneities and the purities of the components salts of all the samples are very high. This facts have already been proved by the comparison of the high-analysis mixed fertilizers with the low-analysis ones (3).

Further, considerable differences were observed both in the states of composition and the rates of composition of their chemical constituents in each sample. This seems to be due to the differences in the raw materials employed and the manufacturing methods of these samples. These differences are thought to exert very marked influences on the availabilities of these sample.

Some examinations have been made to clarify the availability of the high-analysis mixed fertilizers, which treated the influence of the form of ammonium phosphate that is a main chemical component of the mixed fertilizers on the availability of them. These ammonium phosphates were examined by separating into the forms of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, respectively.

Okuda, *et al.* (4) (5) examined various phosphates for the absorption by and the movement in soils and showed that $(NH_4)_2HPO_4$ was less absorbed by and more movable in soils than other phosphates. From these evidences, the form of $(NH_4)_2HPO_4$ seemes to have a higher availability by fertilizing situation. Hamamoto, *et al.*(6) obtained the results that the form of $(NH_4)_2HPO_4$ has a higher availability than other phosphates by the experiment of the similar point of view as that of Okuda, et al. The present writers(7) have been examining the behavior of phosphates in soils and recognized that the form of $(NH_4)_2HPO_4$ has a little higher

rate of diffusion and a somewhat less reaction rate of phosphate fixation than other phosphate.

Thus the form of $(NH_4)_2HPO_4$ is proved to be highly effective in various points. However, these results were obtained from the reaction of phosphates with soils. Therefore, further examinations are required on the absorption of phosphorus and its utilization by plants in relation to the forms of phosphates.

Summary

Chemical properties of the high-analysis mixed fertilizers were examined to clarify the reality of the factors affecting the availabilities of the high-analysis mixed fertilizers by the x-ray diffraction analysis and the polarization microscopic observation. The results indicated that the homogeneities and the purities of chemical components of the high-analysis mixed fertilizers were higher than those of the low-analysis ones, and the raw materials employed for manufacturing the high-analysis mixed fertilizers were hardly detected in the products. While, considerable differences were observed both in the states of composition and the rates of composition of the chemical constituents for each sample. These differences are concluded to be one of the main factors affecting the availabilities of the high-analysis mixed fertilizers.

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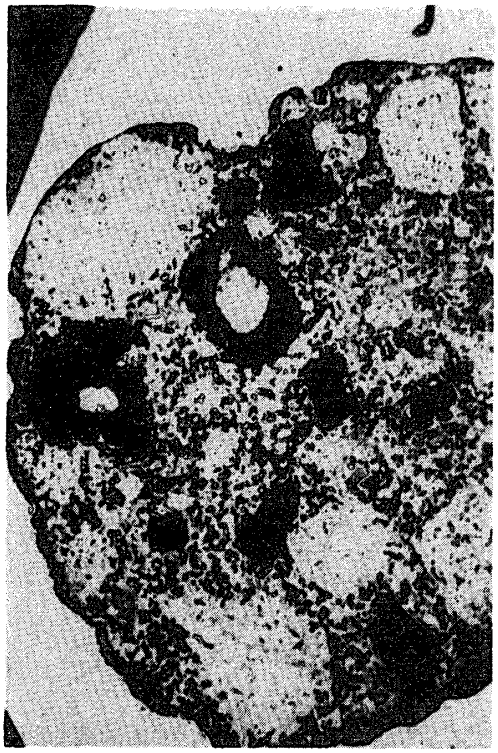
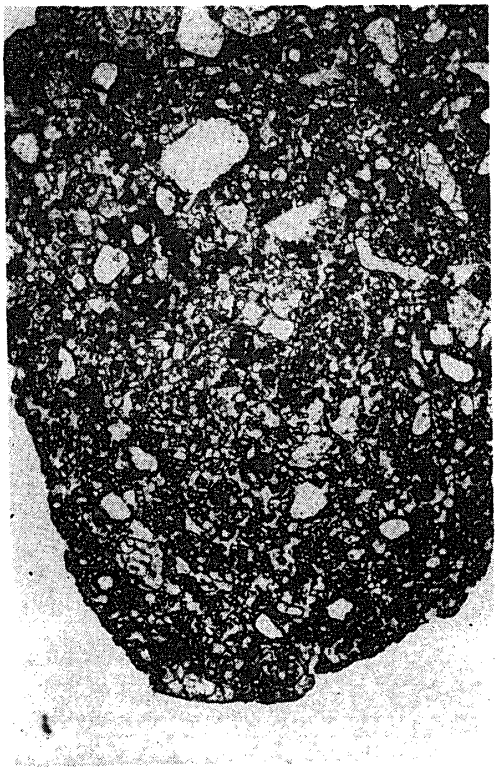


Photograph 1. (×100)

Photograph 2. (×100)

Photograph 3. (×100)



Photograph 4. (×100)

Photograph 5. (×100)

Photograph 6. (×100)

Photograph 7. (×100)